

Monte Carlo Study of Short-Range Order and Displacement Effects in Disordered CuAu

O. Malis, K. F. Ludwig, Jr.
Boston University, Boston, MA.

D. L. Olmsted, B. Chakraborty
Brandeis University, Waltham, MA.
 (February 1, 2008)

The correlation between local chemical environment and atomic displacements in disordered CuAu alloy has been studied using Monte Carlo simulations based on the effective medium theory (EMT) of metallic cohesion. These simulations correctly reproduce the chemically-specific nearest-neighbor distances in the random alloy across the entire $\text{Cu}_x\text{Au}_{1-x}$ concentration range. In the random equiatomic CuAu alloy, the chemically specific pair distances depend strongly on the local atomic environment (i.e. fraction of like/unlike nearest neighbors). In CuAu alloy with short-range order, the relationship between local environment and displacements remains qualitatively similar. However the increase in short-range order causes the average Cu-Au distance to decrease below the average Cu-Cu distance, as it does in the ordered CuAuI phase. Many of these trends can be understood qualitatively from the different neutral sphere radii and compressibilities of the Cu and Au atoms.

1. INTRODUCTION

Understanding the detailed structure of disordered metallic alloys continues to be an experimental and theoretical challenge. Particularly interesting are alloys in which there is a significant mismatch in atomic size. Intuitively, it might be expected that the distances between nearest neighbor pairs in an alloy with large atoms (A) and small atoms (B) would follow a simple relationship $r_{AA} > r_{AB} > r_{BB}$. However, x-ray and neutron diffuse scattering experiments indicate that the behavior is more complex and that there are correlations between chemical ordering tendencies and pair distances (Jiang, Ice, Sparks, Robertson and Zschack 1996). Unfortunately, our general understanding is limited by the statistical nature of the scattering process – typically only average pair distances and chemical coordination numbers can be determined by these methods. They do not provide information about the relationship between local displacements from ideal lattice sites and the local degree of short-range order. Using an effective medium theory (EMT) energy calculation (Jacobsen, Norskov and Puska 1987), we present here a detailed Monte Carlo (MC) study of the correlation between local order and displacements in equiatomic disordered CuAu (12% size difference). EMT is a semi-empirical approach belonging to the category of embedded atom methods, and is based on Density Functional Theory (Jacobsen et al. 1987). These simulations offer the advantage of giving access to individual atoms and their local chemical environment, thus providing information complementary to experiment. They exhibit clear correlations between local chemical environment and displacements in disordered CuAu alloy.

At 50-50 at.% concentration CuAu has two first order phase transitions. Above 683K the stable phase is a FCC disordered phase. Below 658K the stable phase CuAuI is an ordered $L1_0$ phase with a 7% tetragonal distortion. Between those two temperatures the stable phase is a long-period superlattice, CuAuII, with a modulation wavevector perpendicular to the ordering wavevector. The wavelength of the periodic anti-phase boundaries is ten times the size of the underlying ordered cell.

2. MONTE CARLO SIMULATIONS BASED ON EFFECTIVE MEDIUM THEORY

2.1. Simulation Model Details

First principles calculations of the effects of atomic displacements on alloy phase stability have often been based on effective Ising models where the positional degrees of freedom are integrated out at zero temperature (Lu, Laks, Wei and Zunger 1994, Wolverton and Zunger 1995). Finite temperature simulations involving both configurational and positional variables have been possible only with computationally efficient empirical potentials (Dunweg and Landau 1993, Polatoglou and Bleris 1994, Silverman, Zunger, Kalish and Adler 1995). The advantage of a direct simulation over simulations based on effective Ising models is that they yield detailed information about the nature of atomic

relaxations and the coupling between configurational and positional degrees of freedom: information which is hidden in higher order correlation functions of effective Ising models. These considerations led us to investigate the role of atomic displacements in Cu-Au alloys using the EMT formalism. Though EMT is not a first-principles approach, it is a useful model which captures some essential features of metallic binding.

A number of researchers have found that EMT can reproduce well the bulk and surface properties of many pure metals (Jacobsen 1988). EMT-based calculations have also been successfully applied to investigate equilibrium and kinetics properties of Cu-Au alloys. Monte Carlo simulations using the EMT have correctly reproduced the order-disorder transitions in the Cu-Au phase diagram (Xi, Chakraborty, Jacobsen and Norskov 1992). This work illustrated the importance of going beyond cubic fixed-lattice models to include tetragonal distortions (Xi et al. 1992) and atomic displacements (Chakraborty 1995). In addition, EMT has been used to construct an atomistic Landau theory of the alloy (Chakraborty and Xi 1992) which was able to predict qualitatively the stability of the modulated phase CuAuII in a narrow temperature range. Langevin simulations of the ordering kinetics using the Landau model were recently found to be in qualitative agreement with experimental x-ray results (Elder, Malis, Ludwig, Chakraborty and Goldenfeld 1998).

The EMT formalism provides a structure for systematically constructing interatomic potentials in metallic systems where simple pair potentials are known to be inadequate. These potentials belong to the same category as embedded atom potentials (Daw, Foiles and Baskes 1993), however, the details of the construction are different (Jacobsen et al. 1987). The EMT interactions involve parameters characterizing atoms in specific environments; for example, the spatial extent of the electron density distribution around a Cu atom embedded in an electron gas of given density (Jacobsen et al. 1987). In principle, these parameters can be obtained from *ab initio* calculations based on DFT. However, in its application to the Cu-Au alloys (Xi et al. 1992), a semi-empirical approach has been adopted where the atomic parameters are obtained from fitting to the ground-state properties of the *pure* metals and an additional parameter, which enters only in the description of an alloy, is obtained by fitting to the formation energy of CuAu (Stoltze 1997).

We performed MC simulations of CuAu in the canonical ensemble using the EMT approach. In our MC implementation the Metropolis algorithm is used to determine the acceptance/rejection of 3 different kinds of system changes: the interchange of Cu and Au atoms, the displacement of individual atoms from their “ideal” lattice sites, and the size of the global lattice constants. The candidate atomic displacements are chosen randomly in a box whose size is adjusted to optimize the MC acceptance rate. The atomic displacements are due both to thermal vibrations and to “size effects”.

The simulations are performed using a modified version of the ARTwork simulation package (Stoltze 1997) running on a Silicon Graphics Origin2000 computer system. One full MC step for an N -atom simulation cell (32^3 or 60^3) consists of N attempts to (a) randomly exchange atoms, and (b) change the position of the atoms involved in the exchange followed by one attempted change in global lattice constants. When examining properties of the disordered phase the cubic symmetry is fixed. Typically, the alloy is equilibrated at temperature for 1000 MC steps before the data is stored for processing. The averages are usually taken over 50 configurations saved every 10 MC steps.

2.2. Model Accuracy

Before discussing correlations between local chemical order and atomic displacements in our Monte-Carlo simulations of disordered CuAu, we examine the accuracy of the EMT model. The model predicts the correct Cu_3Au , CuAu and Au_3Cu regions of the phase diagram. For the 50-50 composition studied in detail here, previously published EMT simulations which did not allow atomic displacements found (Xi et al. 1992) that the model presents a first order phase transition at approximately 708K between the cubic disordered phase and the tetragonal ordered phase. The ratio of the lattice constants in the ordered phase c/a is 0.94 and agrees well with the actual value of 0.93. In the new simulations reported here, atomic displacements are allowed, but the transition remains first order in accord with experiment. The jump of the long-range order parameter at the phase boundary is 0.94. In addition, the ratio of the lattice constants c/a in the ordered phase remains 0.94. However the transition temperature is considerably lowered by the inclusion of atomic displacements to approximately 430K. Since displacements due to both thermal vibrations and the “size effect” would be expected to preferentially lower the free-energy of the disordered phase, the drop in transition temperature is not surprising. Thus the inclusion of atomic displacements decreases the agreement with the experimental transition temperatures when using the parameters of Xi et al. 1992. As mentioned above the alloy parameter entering the EMT model was obtained by fitting to the CuAu formation energy without incorporating displacements. Therefore it would be possible to improve the current model by adjusting the EMT parameters. However, for consistency with the previously published simulations, we chose to keep the parameters from Xi et al. and to scale all temperatures with respect to the new transition temperature.

The local chemical order and atomic displacements in disordered alloys are often measured by diffuse x-ray or neutron scattering. For comparison, we calculated the x-ray diffuse scattering intensity for the EMT model by Fourier transformation for several effective temperatures just above the phase transition. A typical diffuse scattering in the $(hk0)$ reciprocal plane calculated from a simulation 2.7% above the transition temperature is presented in Fig.1. The asymmetry of the diffuse scattering around the superlattice points is due to atomic displacements (Borie and Sparks 1971). Though not easy to see on the scale of the plot, the simulated peaks exhibit the anisotropic four-fold splitting observed in experiment (Hashimoto 1983, Malis, Ludwig, Schweika, Ice and Sparks 1998). This splitting, which is due to correlations extending well beyond a few unit cells, is reminiscent of that produced by the long-period superlattice of CuAuII. Simulations at several temperatures in the disordered phase reveal that the superlattice peaks grow relatively slowly with decreasing temperature, in accord with experimental observation (Malis et al. 1998).

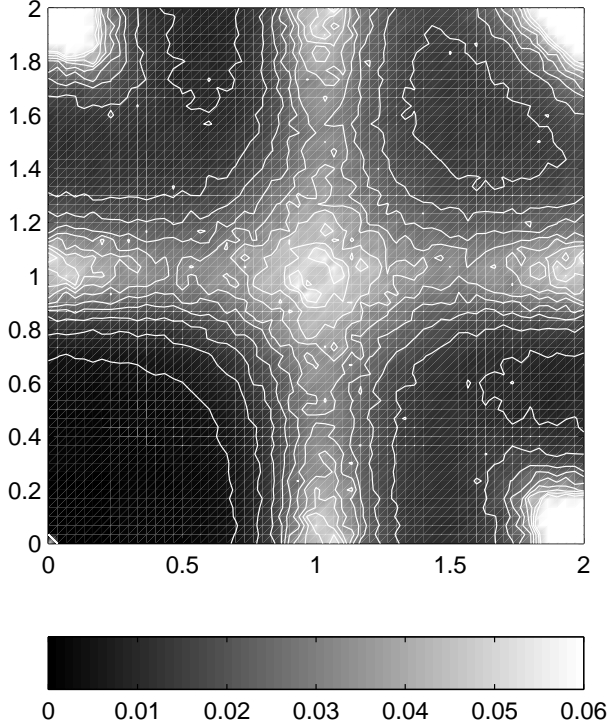


FIG. 1. Diffuse scattering intensity in the $(hk0)$ reciprocal plane from a 60^3 atom simulation of CuAu 2.7% above the transition temperature. The intensity is normalized to $N^2 x_{Cu} x_{Au}$. f_{Cu} and f_{Au} were considered constant and taken to be 26 and 72, respectively.

Metcalf and Leake (Metcalf and Leake 1975) have reported a study of the local chemical order in CuAu alloy as measured by x-ray diffuse scattering. They analyzed their experiments in terms of short-range order parameters α_{lmn} which measure the average number of like/unlike neighbors surrounding an atom in a given shell (Borie and Sparks 1971):

$$\alpha_{lmn} = 1 - \frac{P_{AB}^{lmn}}{x_B} \quad (1)$$

Here P_{AB}^{lmn} is the probability of having a B atom at the (lmn) lattice site if there is an A atom at the origin. In a completely random alloy α is zero. Positive values of α indicate that the corresponding shell is mainly occupied by atoms of the same kind as the atom at the origin. If α is negative the number of unlike neighbors is dominant. For comparison we have calculated the simulated α_{lmn} directly in real space at an effective temperature 2.7% above the phase transition. The calculated values are compared with those from Metcalf and Leake in Table I. The simulated values of the SRO parameters for the first two coordination shells are 2.5% and 10% lower than the values reported by Metcalf and Leake for a sample at a comparable temperature (700 K). Given uncertainties in the accuracy of

the experimental α 's¹ this close agreement may well be fortuitous. The simulations also correctly predict that the magnitude of the third neighbor correlations drops by approximately an order of magnitude compared to those for the two nearest shells. However, the small remaining correlation is incorrectly predicted to be positive for this shell. As a result, the tails of the simulated diffuse scattering peaks shown in Fig. 1 are less symmetric than is the actual case in the alloy. Nonetheless, we can conclude that the degree of local order predicted by the EMT Monte-Carlo model is quite reasonable.

Frenkel et al. (Frenkel, Stern, Rubshtein, Voronel and Rosenberg 1997) have used EXAFS to measure the average nearest neighbor distances in $\text{Cu}_x\text{Au}_{1-x}$ alloys with random atomic arrangements at 80 K. To better test the accuracy of the EMT Monte-Carlo simulations, we performed simulations of a random CuAu alloy quenched to an equivalent temperature and determined the average nearest-neighbor distances for the Cu-Cu, Cu-Au and Au-Au pairs. These are shown in Fig. 2. At all compositions the simulated distances agree with the EXAFS measurements within the experimental uncertainty. Interestingly, both the EXAFS data and our simulations show that the average Cu-Au distance is very close to the Cu-Cu distance and significantly less than the Au-Au distance. Moreover, our simulations predict a crossover of the Cu-Cu and Cu-Au distances near 60% Au concentration, with the Cu-Au distance being the smallest pair distance above this concentration. This is in agreement with first-principles calculations of Ozolins et al. (Ozolins, Wolverton and Zunger 1997). It is noteworthy that the strong concentration dependence of the relative Cu-Cu and Cu-Au distances is larger than expected from compressible Ising models incorporating simple elastic energy and displacement-spin coupling terms (Chakraborty 1995).

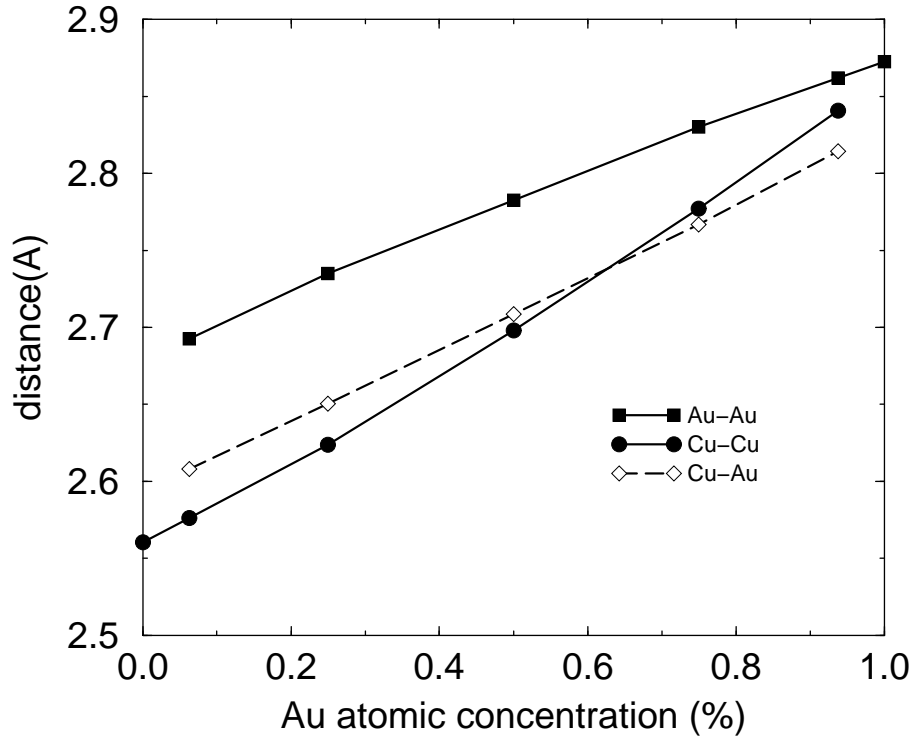


FIG. 2. Concentration dependence of the average Cu-Cu, Au-Au and Cu-Au distances in a random alloy at low temperature. The system size for these simulations was 2048 atoms.

The behavior of nearest-neighbor distances, shown in Figure 2, can be rationalized on the basis of the EMT description of cohesion. In this description, the Au atoms have a larger neutral-sphere radius (the “size” in EMT)

¹Metcalf and Leake used a very approximate scheme to eliminate the thermal diffuse scattering, which is quite large. Moreover, they ignored second-order static displacements, which can contribute significantly to the scattering in their wavevector range. Direct evidence of the limited accuracy of their results is that their α_{000} values, which should by definition be unity, are 26-39% too high.

than the Cu atoms (Jacobsen et al. 1987). Moreover, Au is less compressible. In the simplest approximation, we can view the increase in nearest-neighbor distances with increasing Au concentration as a traditional steric effect associated with the larger EMT “size” of Au atoms. Though this trend is definitely observed in Figure 2, the rate of increase is different for the three different types of chemical bonds. This can be attributed to the difference in compressibilities of Cu (lower bulk modulus – $B_{Cu} = 14 \times 10^{10}$ Pa) and Au (higher – $B_{Au} = 17 \times 10^{10}$ Pa). Although there is some bowing present in the Cu-Cu line, it largely follows the changing lattice parameter with increasing Au content (note that the Cu-Cu pair distance extrapolates to the Au-Au distance at the highest Au concentrations – i.e. to the pair distance in pure Au). Thus the relatively higher compressibility of Cu atoms allows the Cu-Cu distances to follow the “average” lattice with changing concentration. The relative incompressibility of the Au atoms, however, prevents the average Au-Au distance, and the Cu-Au distance, from changing as much with concentration. Within the EMT model, the relative compressibilities can also be related to the more rapid falloff of the electron density around a Au atom than around a Cu atom at typical interatomic distances.

3. CORRELATIONS BETWEEN LOCAL ENVIRONMENT AND DISPLACEMENTS

Though random alloys exhibit no global short-range order, the constituent atoms nonetheless experience stochastic variations in their nearest-neighbor environments. Therefore, in order to investigate the relationship between local environment and pair distances, we have calculated the average interatomic distances in the random equiatomic CuAu alloy as a function of the number of nearest-neighbor Au atoms. That is, we have divided the atoms in the random CuAu alloy into 12 groups – each member of the group has the same number of Au nearest-neighbors. We have then calculated the average Cu-Cu, Cu-Au (Cu being the central atom), Au-Cu (Au being the central atom) and Au-Au pair distances in each group. The results are shown in Figure 3(a). There is a strong relationship between local environment and pair distances. The trends with increasing Au in the local environment are qualitatively similar to those seen in Figure 2 with increasing overall Au concentration. Clearly, even in a random alloy at a fixed concentration, the intuitive idea of atomic “size” has limited meaning.

TABLE I. Comparison of the short-range order parameters α_{hkl} obtained from a simulation 2.7% above the transition temperature with the experimental values (Metcalf and Leake 1975) for a quench from 700K (2.5% above the true transition temperature). The last column shows the values for perfectly ordered CuAu.

hkl	simulation	experiment	ordered CuAu
000	1.0000	1.263	1.00
110	−0.1825	−0.187	−0.33
200	0.2069	0.230	1.00
211	0.0226	−0.013	−0.33
220	0.0484	0.109	1.00
310	−0.0557	−0.029	−0.33

TABLE II. Simulated nearest-neighbor relative displacements $r_{AB} = (d_{AB} - d_0)/d_0$, where d_0 is the average distance, at a temperature 2.7% above the transition temperature and infinite temperature (random alloy), respectively.

pair	finite temperature	random configuration
α_{110}	−0.182	≈ 0
Cu-Cu	0.0015	−0.0092
Au-Au	0.0171	0.0223
Cu-Au	−0.0016	−0.0051

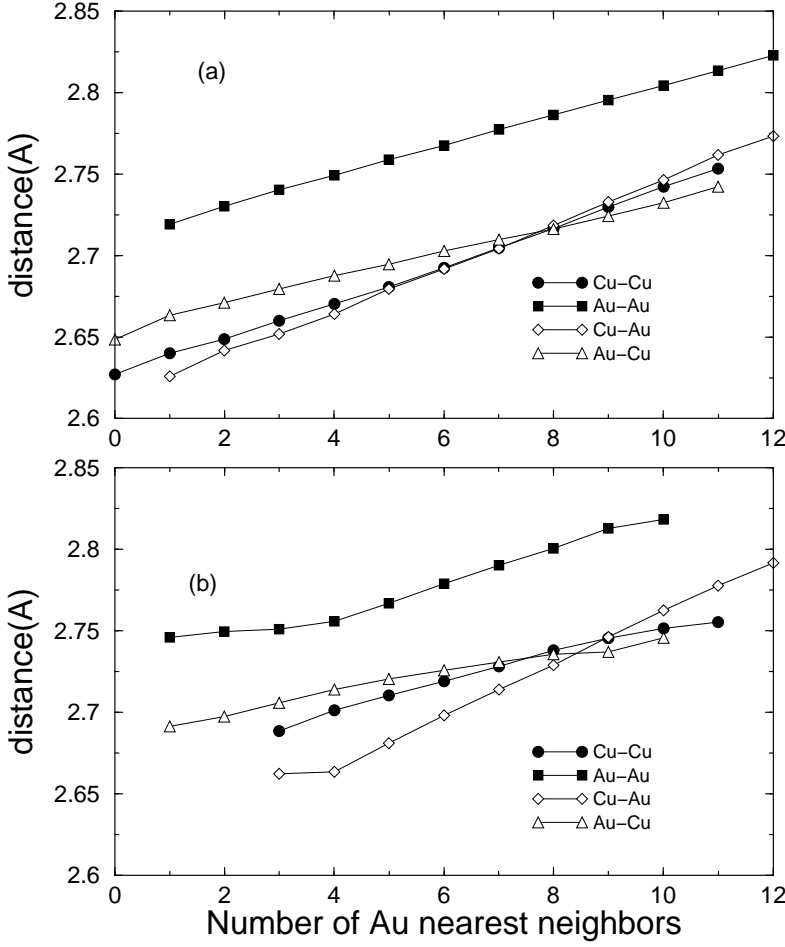


FIG. 3. Dependence of the Cu-Cu, Au-Au, Cu-Au (Cu central atom) and Au-Cu (Au central atom) nearest-neighbor distances on the number of Au nearest neighbors in (a) a random equiatomic CuAu alloy at low temperature and (b) in the same alloy with short range order 2.7% above the transition temperature.

In order to better understand the relationship between local environment and displacements in a non-random alloy, we studied in detail a simulated equiatomic CuAu alloy annealed at a temperature 2.7% above the ordering transition to produce short-range order. In direct contrast to the case for random equiatomic alloys, the overall average Cu-Au distance is shorter than the overall average Cu-Cu distance (table II). Thus the development of short-range order has changed the average pair distances. Figure 3(b) shows how the average Cu-Cu, Cu-Au, Au-Cu and Au-Au pair distances vary with number of Au nearest-neighbors. Comparison with the equivalent Figure 3(a) for a random alloy shows that the overall trends remain qualitatively similar but the short-range order causes quantitative changes.

Another way of examining the data from the alloy with short-range order is to define a local α_{110} for each atom – i.e. the number of like nearest neighbors minus the number of unlike nearest neighbors divided by the coordination number. Figure 4(a) shows the systematic relationship between the local “order” as measured by this α_{110} and the interatomic distances. Here we have grouped together the Cu-Au and Au-Cu distances. Figure 4(b) shows also the histogram of local α_{110} values. For atoms with large positive values of α_{110} , i.e. a large fraction of like nearest neighbors, the relation between like and unlike pair distances follows the simple expectation that $d_{Cu-Cu} < d_{Cu-Au} < d_{Au-Au}$. However, for lower and negative values of α the Cu-Au distance is the smallest of the three. Moreover, the Au-Au distance decreases and begins to approach the Cu-Cu distance, which itself increases with decreasing α . The behavior is very suggestive of the relationships between nearest neighbor distances in the ordered CuAuI phase - i.e. $d_{Cu-Cu} = d_{Au-Au} > d_{Au-Cu}$. It can also be seen from Figure 4 that the development of short-range order, i.e. an increase in the number of atoms with a negative α , in the alloy leads to a decreasing average Cu-Au distance relative

to the average Cu-Cu distance. This partly explains why $d_{Cu-Au} < d_{Cu-Cu}$ in the equiatomic alloy with short-range order but $d_{Cu-Au} > d_{Cu-Cu}$ in the random alloy.

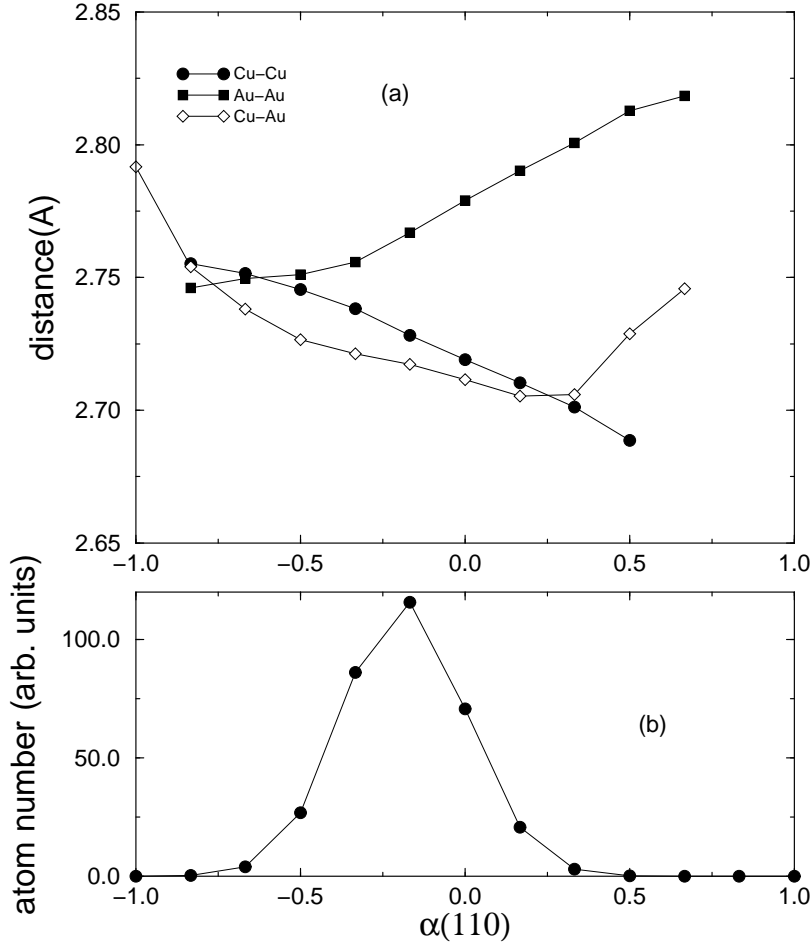


FIG. 4. (a) Dependence of the Cu-Cu, Au-Au and Cu-Au nearest-neighbor distances on the local coordination number α_{110} 2.7% above the transition temperature. The error bars are smaller than the size of the symbols. (b) The distribution of local α_{110} values.

We studied closely the atoms positioned in a local chemical environment similar to the environment in the ordered phase, i.e. having 4 like and 8 unlike nearest neighbors (i.e. local $\alpha_{110} = -0.33$). In the ordered phase the 4 like neighbors occupy one of the cubic planes passing through the center atom while the 8 unlike atoms occupy the other 2 planes. In the simulation we found that approximately 10% of the atoms with 8 unlike nearest neighbors are actually in a geometrically “ordered” environment. However, the occurrence of this configuration is considerably higher than random. Figure 5 contrasts the occupation probabilities in the planes for the random case and that observed in the EMT simulations. It is instructive to focus on those atoms in a geometrically “ordered” environment (as well as chemically ordered environment) and define a local distortion as the deviation from unity of the ratio of the average A-A distance to the average A-B distance around that atom. The average local distortion around Cu atoms in the simulation is approximately 1.5%, slightly higher than the average around Au atoms (0.4%). Both values are much smaller than the 3% that would be predicted by the tetragonal distortion occurring in the ordered structure.

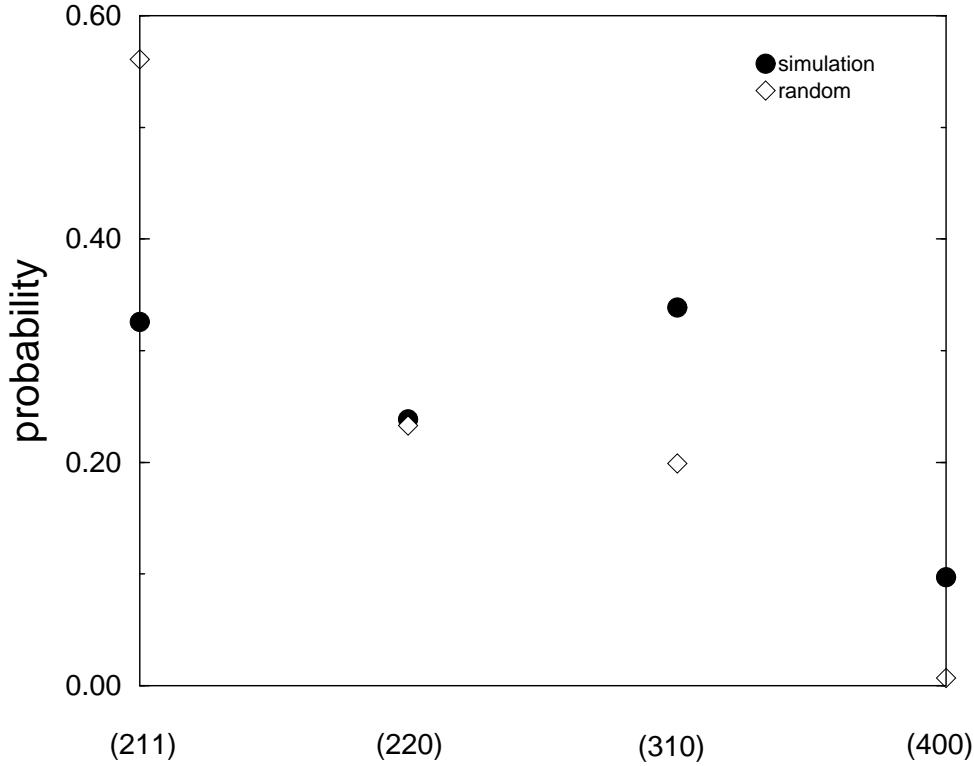


FIG. 5. Probabilities of finding the 4 like nearest neighbors of those atoms with $\alpha_{110} = -0.33$ distributed in the 3 surrounding planes at the simulated temperature. Also shown are the random probabilities.

4. CONCLUSIONS

An important advantage of real space simulations is that they permit a direct examination of the relationship between local chemical environment and atomic displacements. These simulations show a strong correlation between nearest-neighbor environment and interatomic distances in disordered $\text{Cu}_x\text{Au}_{1-x}$, even in random alloys. Higher Au concentrations in the local environment lead to a decrease of Cu-Au distances relative to Cu-Cu distances. In equiatomic CuAu alloys with short-range order, these trends remain qualitatively similar. The increased local “order” causes a decrease in the average nearest-neighbor Cu-Au distance and a partial convergence of Cu-Cu and Au-Au distances, reminiscent of the local structure in the ordered CuAuI phase. The intuitive concept of “size” has limited usefulness in understanding these trends. We anticipate that such correlations between local environment and displacements are common in disordered alloys, particularly those having components with large atomic size differences.

ACKNOWLEDGMENTS

We would like to acknowledge useful discussions with C. J. Sparks and W. Schweika. This work utilizes the resources of the Boston Univ. Center for Computational Science and was supported by NSF grant DMR-9633596. B. C. would like to acknowledge numerous discussions with Per Stoltze regarding the ARTwork program. The work of B. C. and D. O. was supported in part by the DOE grant DE-FG02-ER45495. B. C. would also like to acknowledge the hospitality of ITP, Santa Barbara, where some of this work was performed. B. C. would also like to thank Jens Norskov for suggesting the incompressibility argument.

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